COW MANURE AND BIOWASTE AS A BIOGAS SUBSTRATE
A REVIEW

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Abstract

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Tiivistelmä/Referat – Abstract

The research of this thesis was focused on anaerobic digestion of cow manure mixed with different types of biowaste, especially those material that are available in Finland. The research was conducted by search, collection, and analysis of different data in literature. Topic of the thesis was predetermined by the Co-Creation Lab project of Helsinki Institute of Sustainability Science (HELSUS), which was seeking solution to achieve carbon neutral cow milk production. The solution was co-approached by three participants conducting thesis from technological, economical, and legislative points of view, in which I was responsible for writing mainly the technological part, and general findings in economic efficiency and legislative terms by the other two co-creators were also included in this thesis.

The research was mainly related with the whole cycle of biogas production, including basics about anaerobic digestion (AD), applications of the biogas and digestate as a product and by-product of AD. Substrates for AD were researched with a focus to find the best combination of cow manure (CM) and biowaste in regard with methane yield outcome, especially a mixture of CM and silage waste that suits the cow farming situation in Finland. Methane yields for mono-digestion of various types of biowaste and co-digestion of CM with different biomass were collected and analyzed. Premises for biogas plant establishment were researched briefly, including facility composition, and consideration of feasibility and raw material availability.

CM with grass containing 75% timothy and 25% meadow fescue grass at 70%:30% mixing ratio could be the best combination of CM: grass co-digestion, followed by 0.5:0.5 mixed CM and perennial ryegrass. Furthermore, CM mixed with food waste at 52:48% ratio could be the best combination among co-digestion of CM with biowaste other than grass, followed by CM and food waste mixed with 68%:32% ratio, and CM with oat straw mixed at 1:2 ratio could be a considerable combination of CM and crop waste.

Avainsanat – Nyckelord – Keywords

Anaerobic digestion (AD), cow manure (CM), waste, co-digestion, biogas, methane.

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Nomenclature

AD	anaerobic digestion
C	carbon
CH_4	methane
CHP	combined heat and power
CM	cow manure
CO_2	carbon dioxide
CSTR	continuously stirred tank reactor
d	day
DD	dry digestion
DM	dry matter
FVW	fruit and vegetable waste
FW	food waste
H	hydrogen
H_2	molecular hydrogen
H_2S	hydrogen sulphide
ha	hectare
KW	kitchen waste
kWh_{el}	kilowatt hours electrical energy
m^3	cubic meter
MC	maize cobs
Mg	megagram
MG	maize grains
MS	maize straw
N	nitrogen
NH_3	ammonia
°C	degree Celsius
O	oxygen
OS	oat straw

P	phosphorus
PPS	paper and pulp sludge
PRG	perennial ryegrass
RC	red clover
RS	rice straw
SBT	sugar beet top
SDD	semi-dry digestion
SG	switchgrass
SNG	substitute natural gas
SOFC	solid oxide fuel cell
SS	sewage sludge
T&MF	timothy and meadow fescue
TS	total solids
TWh	terawatt hour
TWh a^{-1}	terawatt-hour per year
VS	volatile solids
VS_a	volatile solids added
WD	wet digestion

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1. Introduction

Anaerobic digestion (AD) has been used world widely to recycle organic waste (biowaste) and to produce biogas to generate energy, in small scale such as domestic biogas producing tanks, and large scale like biogas power plants. According to the European Biogas Association (EBA 2019), by the end of 2017, biogas was produced 200 TWh a^{-1} (terawatt-hour per year), and this amount of biogas is equal for 4% of the inland gas consumed within EU. Furthermore, more than 65 TWh European electricity was generated from biogas in 2017, which was equal to annual power consumption of Austria (EBA 2019). Besides biogas, the by-product - AD process slurry - known as a digestate, can be returned to soil to be used as fertilizer due to its considerable content of residual organic-carbon and richness of nutrients (Alburuerque et al. 2012, Pawlett et al. 2018).

Diverse types of biowaste such as animal manure, crop production residues (such as straw and stalk), grass, and food waste and mixtures of them have been studied in order to optimize AD condition, substrate combination, enzyme or bacterial inoculation, and the biogas yield finally. As the major livestock manure contribution, cow manure (CM) is considered as an excellent raw material to be mixed with other types of biowaste for co-digestion (Huang et al. 2016, Achinas et al. 2018). Biowastes that can be utilized as the co-digestion substrate with CM include energy crop, grass, food waste, straw, and sewage sludge (Cropgen 2006, Jagadabhi et al. 2008, El-Mashad and Zhang 2010, Wang et al. 2016).

Besides nutrient circulation and energy generation, a CM-based biogas plant can also reduce overall carbon footprint of livestock farming, in addition to reducing herd size which is the main solution of greenhouse gas (GHG) emission reduction for livestock farming suggested by Lötjönen et al. (2020). According to a specific environmental assessment of milk carbon footprint (Harmoinen Robert, University of Helsinki, Finland, email message to author, 27 March 2020), replacement of fossil diesel by biomethane could reduce carbon footprint by 12%, and AD of CM could reduce manure storage carbon footprint by 89%, fertilizer production 30%, and indirect nitrous oxide emission 77%. Therefore, by replacing diesel by biomethane, the overall mitigation of carbon footprint of milk could be estimated to be 15% (Harmoinen Robert, University of Helsinki, Finland, email message to author, 27 March 2020).

In this thesis following topics are covered in relation with biogas production of CM being mixed with various types of biowaste. Factors of the AD process to maximize the biogas yield were introduced briefly to get a general insight about biogas production. Applications of AD product (biogas) and by-product (digestate) were researched for post-production practices. Methane yields of mono- and co-digestion of different types of biomass were analyzed, with recommendation of optimal co-substrates available in Finland. Availability of biomasses suitable for anaerobic co-digestion with CM in Finland was researched through geological figures. Optimal mixture of CM with different co-materials from biowaste available in Finland was analyzed through several co-digestion results. Economic efficiencies of different types of biogas plants and legislative regulations related with CM-based biogas plants researched by the other two co-creators were also referred briefly in this thesis.

This thesis is an outcome of a Co-Creation Lab project of Helsinki Institute of Sustainability Science (HELSUS), which is a cross-faculty research unit in sustainability science organized by The University of Helsinki. This project involved societal actors of various aspects with different research backgrounds to gather with university students, to discover innovative thoughts and solutions for their common concerns. I was responsible for the technical research part, David Huisman Dellago was responsible for the economical point of view, and Mirjami S.P. Ylinen was responsible for the legislative aspect of the project, through informative and practical supports from the Valio Group, under guidance of supervisors from the university and HELSUS. The purpose of the project of this group was to establish a solution for a carbon neutral milk chain, with a focus on generating biogas by recycling cow manure and other types of biowaste available in Finland.

2. Research Objectives

Main objective of the research was to analyze the methane production potential from mixtures of CM and different types of organic waste materials. Sub-objectives of the research were several aspects related with the whole biogas production cycle, from beginning of anaerobic digestion process, to application of the end product and by-product. The objectives were divided into different parts including studying the parameters of the biogas process important for co-digestion of CM and biowaste, analyzing biogas yield of mixtures of CM and typical biowastes in Finland, and discussing feasibility of establishment of a biogas plant in different regions within Finland.

Production process researched in this study was AD by series of biochemical reactions performed by various types of bacteria (microbes) with different characteristics that can be classified into different groups based on the conditions to secure their liveness and biodegradation of organic matters. For obtaining maximal methane yield at the final stage, environmental factors crucial for an AD process were also researched with recommended value ranges. Applications of the product (biogas) and by-product (digestate) were also introduced to find outgoing pathways for biogas plants after methane production. Co-digestion of CM along with other biomasses including crop straw, grass, food waste, and so forth was analyzed to find suitable co-substrates for a CM-based biogas plant, and grass was the main focus since it suits the practical situation of cow farming in Finland. Feasibility of establishing a biogas plant was also researched, considering premises such as raw material availability, power installation design, and methane yields of different substrates which were analyzed weightily. Mono-digestion and co-digestion were both researched to find substrates with more methane yield in faster speed. General findings about economic efficiencies of biogas plants facilitated with equipment for different applications of methane and legislation related with CM-based biogas plants from production to application of product and by-product, which were researched by the other two co-creators were also introduced in this thesis.

3. Literature Review

This thesis was written based on literature data and information about biogas production process, and utilization of its product and by-product. Raw materials used for the process, feasibility of establishing a CM-based biogas plant in different regions within Finland were also researched since they are essential for production of biogas. Economical efficiencies of biogas plants with different facilities, and legislation terms related with biogas plants researched by the other two co-creators were also introduced briefly.

3.1. Anaerobic Digestion (AD) Process

AD is a complex process during which almost any type of organic waste can be biologically digested in anaerobic conditions through diverse bacteria consortium to produce mixed gases with high energy potential known as biogas (Lastella et al. 2002). AD can be conducted by digesting single type of substrate known as mono-digestion process, and simultaneously digesting two or more different substrates known as co-digestion process (Zhang et al. 2016). Generally, production of methane during the AD process follows the oxidation-reduction equation (Buswell and Mueller 1952, equation 1) with water involved, based on composition of carbon (C), hydrogen (H), and oxygen (O):

$$C_nH_aO_b + (n - a/4 - b/2)\ H_2O \rightarrow (n/2 - a/8 + b/4)\ CO_2 + (n/2 + a/8 - b/4)\ CH_4 \qquad (1)$$

3.1.1. Four steps of AD process

The anaerobic digestion of biomass undergoes four phases that turn organics into methane gas and other substances (Maintinguer and Pires 2016, Schnürer and Jarvis 2018, Laiq Ur Rehman et al. 2019). As stated by Maintinguer and Pires (2016), these phases are firstly the hydrolysis phase where the complex molecular substances are hydrolyzed and degraded into simpler and smaller molecular substances such as fatty acids, glucose and amino acids by fermentative bacteria (Figure 1). Secondly, acidogenesis is the phase during which the hydrolyzation products from the previous phase are degraded further into smaller organics such as acetate, butyrate and propionate, along with certain gaseous substances including ammonia (NH_3), carbon dioxide (CO_2) and hydrogen sulphide (H_2S).

Thirdly, acetogenesis is the phase through which the organic products are degraded into substances including acetate, molecular hydrogen (H_2), and CO_2 which will then be utilized in the following phase. Fourthly, methanogenesis is the last phase where the products from the previous phase are converted into methane gas and other products and by-products (Figure 1).

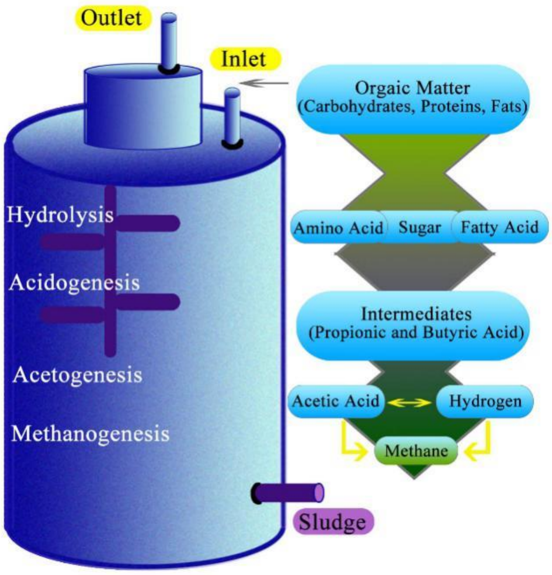

Figure 1. Illustration of anaerobic digestion process. Adapted from Laiq Ur Rehman et al. (2019).

AD of biowaste can reduce GHG emissions by sequestration and application of methane which otherwise may cause higher GHG effect if leaked into atmosphere (Nguyen 2016). It also has other benefits such as improving nutrient recycling possibilities (especially for nitrogen, phosphorus, and potassium), providing biogas for energy production, and providing organic fertilizer for plants with improved quality compared to raw agricultural biowaste (Nguyen 2016). The drawbacks of this technology include environmental sensitivities, COD load restriction, low COD removal rate, high investment requirement, expertise requirement, H_2S generation, possible heavy metal existence, and complexity of economic feasibility (Stuart 2006). As Stuart (2006) stated, anaerobes involved in AD are generally more sensitive to environmental changes and grow and function slower than aerobes, they require stable COD load to perform normally, the insufficient COD removal may require a further step for COD reduction, and if there are heavy metals contained in the substrate, they can hardly be removed during the AD process. Moreover, the corrosive H_2S produced from AD also requires more robust equipment that can be more expensive, and the economic efficiency of the whole digestion cycle relies on complex benefits in addition to energy production including stabilization of the process, nutrient cycle, sale of fertilizer, and so forth.

3.1.2. Classification of AD process

Generally there are three types of AD depending on total solids (TS) content in the substrate, which are low-solids or so called "wet" digestion for substrate containing TS lower than 20%, "semi-dry" digestion with TS around 20%, and high-solids or "dry" digestion for TS higher than 20% (Shahriari et al. 2011). Dry digestion has certain advantages in regard to wet digestion such as less water consumption, lower digestate slurry generation, more concentrated nutrients, higher transportation efficiency and more efficient use of digesters (Zhou et al. 2019). This type of AD also has disadvantages such as difficulty in complete waste mix, and impossibility of achieving optimal bacterial interactions and degrading performance (Shahriari et al. 2011).

For the wet digestion, the substrate is first adjusted to specific TS content, before being fed into the digestion system, and process water may be needed for the dilution which may also dilute the inhibitory substances (Li 2015). In general, addition of water is only needed when water content in the feed materials is inadequate, since cow manure slurry often contains sufficient water (generally TS content around 10%, Seadi et al. 2008) for the digestion (Anti-Pekka Partonen, Valio, Finland, email message to author, 12 March 2020). Wet digestion is generally performed using continuously stirred tank reactors (CSTR) or wet single-pass digesters, where the feedstock can be mixed properly with the installed equipment for mechanical, hydraulic or pneumatic mixing (Li 2015).

3.1.3. Conditions to ensure satisfying biogas yield

There are several environmental factors known to affect biogas yield from AD processes, including temperature, oxygen, pH, and salts (Schnürer and Jarvis 2018). Since different types of reactions are involved during an AD process as mentioned above, the microbial consortium within a biogas production system may contain different groups of microbes, which prefer different ranges of temperature for their survival and growth. Methane producing microbes are sensitive to change of temperature, therefore temperature is considered as the most important factor affecting the AD process (Laiq Ur Rehman et al. 2019). Peak growth rate of psychrophilic (organisms which survive and grow generally at temperature under 15℃, Martin and Hine 2016a) microbes is 4℃; mesophilic (organisms that survive and grow at temperature ranging from 10 to 40℃, Martin and Hine 2016b) microbes 39℃, and thermophilic (organisms which survive and grow typically above 40℃, Martin and Hine 2016c) microbes 60℃. The optimal temperature range for biogas production from AD process is generally around 30 - 40℃ or 50 - 60℃ (Schnürer and Jarvis 2018). AD does take place under psychrophilic condition, but the biogas yield is rather lower than the other temperature ranges (Dhake et al. 2010).

Microbes are categorized into different groups based on their reactions while being in contact with oxygen, and the microbial consortium within a biogas production system may contain strict anaerobes, and facultative aerobes (Schnürer and Jarvis 2018). The microbes that produce methane belong to the strict anaerobe group which grow only with no oxygen present; whereas various strains of fermentative microbes belong to the facultative aerobes which function and grow when oxygen is either available or unavailable (Schnürer and Jarvis 2018). The facultative aerobes activate the aerobic respiration to grow with presence of oxygen, and turn to fermentation if oxygen exhausts, allowing for the biogas production system to tolerate temporary leakages of air (Schnürer and Jarvis 2018), and Montalvo et al. (2016) even reported that a pre-aeration into the biogas production system can improve the hydrolysis process and hence increase up to 211% of the methane yield.

Both the digestion process and its products are directly influenced by the pH value, which has significant effect on growth rate of the microbes within an anaerobic digestion system (Mao et al. 2015). Within a biogas production system, the microbes that are acid-producer can adapt to pH as low as 5, whereas most of the methane-producing microbes prefer neutral pH values to perform with expected yields (Schnürer and Jarvis 2018). However, some of the acidophilic microbes that produce methane have been discovered to be able to still grow with pH as low as 4.7 (Bräuer et al. 2006), and some alkaliphilic microbes that produce methane may grow most rapidly with pH as high as 9.2 (Mathrani et al. 1988). Currently in Sweden there are some biogas production systems performing at pH as high as around 8 (Schnürer and Jarvis 2018), and some that produce methane at pH lower than 6 as exampled in the literature (Savant et al. 2002). Seadi et al. (2008) suggested that the methane production occurs at pH ranging from 5.5 to 8.5, in which the optimal range is from 7.0 to 8.0, and Mao et al. (2015) suggested 6.8-7.4 as the ideal pH range for the whole AD process.

Salts including sodium, potassium, chlorine, and so forth, are considered essential substances for all microbes to perform, and they generally exist in numerous types of substrates within a biogas production system, therefore need no additional supplementation during the AD process (Schnürer and Jarvis 2018). For a specific range of salt content suitable for the biogas production, Yuka et al.

(2016) reported that salt concentration as low as 35 mS cm^{-1} (milli-siemens per centimeter) could decrease methane yield, and so could the concentration as high as 80 mS cm^{-1}. However, since biogas production systems vary in incoming substrates, this range may be different from case to case.

3.2. Applications of AD products

Since AD generates biogas as the main product, and the solid digestion residue (digestate) as the by-product, the applications can be considered from both the gas and solid residue directions. The AD products may be applied directly, or after certain steps of processing, depending on the purposes and requirements of the applications.

3.2.1. Applications of biogas

Based on statistics of most of the literature, biogas consists of 50-75% methane, 25-45% carbon dioxide, and other gasses including water vapour, oxygen, nitrogen, hydrogen, ammonia, and hydrogen sulphide altogether contributing the other minor percentages (Seadi et al. 2008). Biogas has been considered a promising resource for meeting specific energy needs, yet with certain environmental benefits for sustainable development of the globe (Mao et al. 2015). According to The European Biogas Association (EBA, 2018), there are over 17,000 biogas plants functioning in Europe, and more than half of the electricity supplied from these biogas plants is generated by feedstock from agricultural sector. Biogas from AD processes after desulphurization and dehydration, can be utilized for various aspects of purposes including direct combustion and heat generation, generating electricity by combined heat and power (CHP) units, fuel cell utilization, and also being upgraded to biomethane that functions same as natural gas (Baxter et al. 2013).

Generally, biogas can be directly burned in boilers or burners, or combusted in natural gas burners, for producing heat in-situ or through transportation to users, with no need of quality upgrading, and the contamination it generates is less than the other applications (Seadi et al. 2008). However, Seadi et al. (2008) also suggested that for heat production, certain types of processing may be needed for biogas to perform properly, including condensation and removal of particulates, compressing, cooling, and drying. Heat production is the easiest way of utilizing biogas, but in many cases, it is more economic to produce heat from other renewable fuel resources such as wood chips and straw, and need of heat is significantly lower in warmer seasons like summer (Lantz 2012). Therefore, CHP system can overcome these disadvantages by turning some heat into electricity which can be linked to the electric grid with higher economic value, yet with no concern of the need for electricity in any specific season (Lantz 2012). In Germany, CHP is the most common application of biogas (Wu et al. 2016). Biogas first undergoes drainage and dehydration before the CHP conversion, and most of the gas engines constrain content of hydrogen sulphide, halogenated hydrocarbons, and siloxanes to certain limits, and such engines generally produce 35% electricity and 65% heat, with efficiency up to as high as 90% (Seadi et al. 2008). Skovsgaard and Jacobsen (2017) reported that for 100% manure-based plants, annual input conversion from 110,000 to 500,000 tons, could reduce the total unit cost by 6%, and they suggested upgrading biogas to natural gas level to mitigate dependence of local demand and avoid fluctuation of heat demand.

Biogas can be fed into electrochemical devices known as fuel cells which produce electrical energy from chemical energy through certain reaction, and this type of devices are basically comprised of an electrolyte layer connecting with a porous anode and cathode at each side (Seadi et al. 2008). Biogas is fed to the anode compartment of the fuel cell continually, and oxygen contained in the air as an oxidant is fed to the cathode compartment continually as well, to activate an electrochemical reaction at the electrodes, which furthermore generates the electric current (Seadi et al. 2008). Among different types of fuel cells, solid oxide fuel cell (SOFC) is a well-known electrochemical technology for biogas application, because of its high efficiency, less environmental contamination, fuel flexibility, possibility of thermal recovery from high-temperature exhausts, and higher tolerance of fuel contaminants (Suranat et al. 2013, Cuneo et al. 2018). Upgraded biogas known as Substitute Natural Gas (SNG) or biomethane with similar characteristics and uses to natural gas, can be injected into the natural gas grid, and it can also be used as vehicle fuel powered by natural gas (Čermáková et al. 2012). Before being utilized as natural gas alternative for the natural gas grid or vehicle fuel, certain upgrading process is required for the biogas, to remove all of the possible contaminants and carbon dioxide, and purify the methane content to more than 95% , and the upgraded biogas at this stage is also known as biomethane (Seadi et al. 2008). In Sweden, upgrading biogas to vehicle fuel has become the dominant application of the biogas produced from the new and large-scale biogas plants (Lantz 2012). According to the assessment by Wu et al. (2016), the systematic energy efficiencies among CHP, SOFCs and upgrading are compared in the order from CHP (30.4%), and SOFCs (32.9%), to upgrading (46.5%).

3.2.2. Application of AD digestate

The effect of digestate on plant growth enhancement is considered similar to mineral fertilizers (Guster et al. 2005). According to Seadi et al. (2008), digestate has improved homogeneity and nitrogen:phosphorus (N:P) ratio in the composition, also more inorganic N that is straight plant available, and its predictable nutrient content makes it easier to calculate optimal dosage and integration for fertilization planning compared to organic N fertilizers. Digestate to be used as fertilizer requires certain level of quality with essential characteristics such as: declared nutrient content, pH, content of dry and organic dry matter, homogeneity, purity (referring to containing no inorganic substances such as plastic, stones, glass), and sanitization and safety for organisms and the environment (Al Seadi and Lukehurst. 2012). To ensure digestate quality to fit fertilizer use, high quality is required for the feedstock, which mainly comes from animal manure, crops, vegetable by-products and residues, and other wastes generated from agriculture, horticulture, forestry, and so forth (Al Seadi and Lukehurst 2012). AD of manure generally can reduce odour, eliminate weed seeds, degrade certain amount of organic matters contained in the animal manure, make the pumping and applying to the soil easier than the raw slurry; and it also benefits with sanitation, plant burning avoidance, and fertilizer improvement (Smet et al. 1999, Seadi et al. 2008).

3.2.3. Cow manure with no mixing with other substrate

Cattle manure can be applied in mono-digestion for biogas production, due to availability of the fermentation bacteria and richness of biodegradable substances including carbohydrate and lips (Achinas et al. 2018). According to Achinas et al. (2018), wet mono-digestion of CM sample from Netherlands containing 12.13% total solids (TS) produces biogas of 104 m^3 Mg^{-1} VS (normal cubic meters per megagram of volatile solids) that contains 64% of methane under constant mesophilic condition (36 ±1℃) in 24 days, with pH 7.25 at starting point, and 7.02 end point. In an experiment, CM sample from Finland yielded 204±16 m^3 Mg^{-1} VS through wet digestion (TS 4.9±0.1%) in a CSTR system at 35±1℃ for 20 days (Cropgen 2006).

CM contains abundant methanogens that are necessary for producing biogas, but its high contents of lignin and nitrogen may have negative effects to the biogas production processes (Momoh and Anyata

2014). During AD of CM, the free ammonia and volatile fatty acids as by-products of the processes, may interact biochemically and result in stable digestions with lower methane outcome (Angelidaki and Ahring 1993). As reported, in the reactors with pH 7.6, free ammonia (NH_3-N) inhibited 50% methane production at 37℃ when its content reached to 220 mg/l and with the same inhibition rate at 55℃ when its content reached to 690 mg/l (Gallert and Winter, 1997). With pH ranging from 7.4 to 7.6, free ammonia content of higher than 700 mg/L under thermophilic condition higher than 45℃ could decrease methane yield sharply (Angelidaki and Ahring, 1994).

3.2.4. Maize

Currently maize (*Zea mays* L.) is the most commonly fed crop material for producing biogas in Europe (Grieder et al. 2011), with high yields in both dry matter biomass and methane in biogas (Schulz et al. 2018). Generally, maize crop can yield 7,500-10,200 m^3 ha^{-1} methane annually under optimal condition, based on biomass yield ranging from 20,000 to 30,000 kg DM ha^{-1} (Amon et al. 2007). According to the batched experiments by Simona et al. (2015), wet digestion of maize grains (TS 12.6±0.8%) produces 709 m^3 Mg^{-1} VS biogas containing 55.4% methane, dry digestion of stalks (TS 74.5±0.8%) produce 424 m^3 Mg^{-1} VS biogas containing 55.1% methane, and cobs (TS 56.5±0.2%) 380 m^3 Mg^{-1} VS biogas containing 54.4% methane at 40℃ for 40 days.

3.2.5. Grass

Perennial grasses are considered to be better feedstock of biogas production than maize with less GHG emission (throughout the whole cycle from biofuel production to combustion) and agrichemical pollution, lower input requirement, and more biodiversity in the cultivation area (Tilman et al. 2006, Kandel et al. 2013). It has been reported that under optimal condition, perennial grass (species unknown) in Austria could yield 3,200-3,500 m^3 ha^{-1} methane annually, based on biomass yield ranging from 4,200 to 6,400 kg DM ha^{-1} a^{-1} (Amon et al. 2007). Grass Ley – a mixture of 27 weight percent of timothy (*Phleum pretense* L.), 24 weight percent tall fescue (*Schedonorus arundinacea*), 24 weight percent alfalfa (*Medicago sativa* L.), 18 weight percent red clover (*Trifolium pratense* L.), and 8 weight percent chicory (*Cichorium intybus* L.) - in Southern Sweden could produce methane ranging from 290±7 to 340±4 m^3 Mg^{-1} VS through dry digestion with 35% dry matter at 37.5℃ for

30 days (Prade et al. 2019). Sum of weight percent of 27, 24, 24, 18, and 8 is 101, which is over 100%, so there could be some writing error in the original literature. Grass handled with different manners before being fed into a biogas production system, could vary slightly in methane yields, which is explained later in the co-digestion (3.3.2) section.

3.2.6. Straw

Renewable biomass such as vegetable oil, beets, and straw, has been focused world widely in producing hydrogen, biogas, alcohols and so forth, for both supplementing fossil fuels and mitigating environmental pollution (Chandra et al. 2011). With different compositions of organic matters, different types of crop waste generate different yields, for instance maize crop waste produces 338 m^3 Mg^{-1} VS_a (cubic meter per megagram volatile solids added) methane, wheat (*Triticum aestivum* L.) straw 290 m^3 Mg^{-1} VS_a, and rice (*Oryza sativa L.*) straw 302 m^3 Mg^{-1} VS_a in average under optimal condition (Chandra et al. 2011). According to Yuan (2013), rice straw sampled in southern China yielded 178 m^3 Mg^{-1} VS in a specific experiment, although theoretically it could reach to 333 m^3 Mg^{-1} VS through dry digestion with 93.72% TS under mesophilic condition (37±1℃) at pH ranging from 6.8 to 8.0 for 23 days. Wet digestion of sugar beet (*Beta vulgaris* var. saccharifera) tops sampled in southern Finland diluted with distilled water could produce 181±9 m^3 Mg^{-1} VS methane under mesophilic condition of 35±1℃ for 20 days (Cropgen 2006). Wet digestion of oat (*Avena sativa* L.) straw sampled in central Finland diluted with distilled water could produce 138±17 m^3 Mg^{-1} VS methane under mesophilic condition of 35±1℃ for 20 days (Cropgen 2006).

Straw usually has high concentrations of cellulose, hemicellulose and lignin and degrades slowly within AD reactors; therefore it is suggested to break the complex structure before feeding the straw into the digestion system (Schnürer and Jarvis 2018). Generally, straw used for biogas generation is aligned in rows after harvesting, packed into bales and/or made into pellets, and then delivered to biogas plants, where it is heated under certain magnitude of pressure, and undergoes some biodegradation process to break down the biomass through specific types of enzymes (Torben 2011).

3.2.7. Mixed food waste

AD has been suggested to be a reliable measure to manage food waste by producing bio-energy (methane), and both mesophilic and thermophilic conditions are feasible for AD processes of food waste (Zhang et al. 2014). Methane yield from AD of food waste from restaurants, grocery stores and other commercial sources in San Francisco, USA ranged from 353 m^3 Mg^{-1} VS through semi-dry digestion with 28±1.3% TS under mesophilic condition of 35±1℃ with pH around 7.10 for 30 days (El-Mashad and Zhang 2010); to 435 m^3 Mg^{-1} VS through dry digestion with 30.9±0.07% TS under thermophilic condition of 50±2℃ with pH 7.57(±0.13) for 28 days (Zhang et al. 2006). Schnürer and Jarvis (2018) suggested to maintain variety in the food waste composition, to ensure there is no dominant components contained in the substrate, such as quite more meat than vegetables and fruits which may constrain biogas output in the effluent. In addition, unbalanced production and consumption rates of volatile fatty acids during AD often cause issues such as low pH, reduced methanogenesis and upset digesters (Shin et al. 2015).

3.2.8. Sewage sludge

Sewage sludges from different phases of wastewater treatment plants are commonly used for biogas production, though they often contain complex substances which are rather difficult to degrade biochemically (Schnürer and Jarvis 2018). As reported by Lise et al. (2008), AD of sewage sludge has been the major source of biogas, along with a small proportion contributed by solid waste or lignocellulosic substances through fermentation or gasification. Mono-digestion of sewage sludge from municipal wastewater treatment plant could yield 28 m^3 Mg^{-1} VS through wet digestion with 1.45% TS under thermophilic condition (55℃) for 30 days and 255 m^3 Mg^{-1} VS through wet digestion with 2.70% TS under mesophilic condition (35℃) for 35 days (Montañés et al. 2014).

3.2.9. Co-Digestion

Co-digestion, which refers here to AD using co-substrate that most likely improves biogas yield through establishing positive synergism in the medium and supplementing insufficient nutrients by the co-substrates (Mata-Alvarez et al. 2000). Moreover, co-digestion also helps establishing optimal moisture contents of raw material fed into the digester, makes it easier to handle mixed wastes, and increases cost-effectiveness by sharing equipment and facilities; although it may increase transport costs and/or cause issues in coordinating policies related with waste-generators (Mata-Alvarez et al. 2000). In addition, Huang et al. (2016) reported that co-digestion could generate digestate with higher stability than mono-digestion, and considered it an efficient means for improving degradation of the biowastes.

In this study, co-digestion of cow manure mixed with other organic wastes was researched, considering availability of the raw material existing within Finland. Although it is feasible to use sewage sludge as a part of AD substrate, for fertilizer application of the digestate, it is excluded from co-digestion in this study, due to uncertainty of the composition which may bring negative impact to the fertilized plants. The negative impact of sewage sludge is mainly due to presence of certain contaminants such as cadmium, mercury, lead, zinc, drug residue, and flame retardant, which can accumulate into soil with possibility of being transported to plants and even to humans and animals later on (Hannu Mikkola, University of Helsinki, Finland, email message to author, 5 March 2020). Moreover, maize grain is also excluded from the co-digestion, since in this study the main focus is applying biowaste for biogas production. Grass collected from buffer zones of rivers and lakes, grass from nature management fields, waste grass silage (spoiled or surplus feed), could be typical co-digestion material with CM (Hannu Mikkola, University of Helsinki, Finland, email message to author, 5 March 2020), therefore it is included in the AD co-substrate in this study. In addition, biowaste composition may vary in different regions with different types of climates, therefore sampling location is also taken into consideration.

3.3.Biogas plant: inputs and outcomes

Establishment of a biogas plant is in need of comprehensive plan and design regarding incoming raw material, outgoing products, and process of the production. Composition of a biogas plant, feedstock availability, yields of different combinations of the raw materials, economic efficiencies of different scenarios of the plant, and related legislative terms are researched in this section.

3.3.1. Feasibility

Essential premises for establishing an AD based biogas plant are availability of substrate and feasibility of its continuous supply; possibility of using and/or selling the final products including biomethane along with the heat and electricity it could generate or biomethane used as transport fuel, and the by-product known as digestate (Seadi et al. 2008). Different facilities within a biogas plant, raw material accessibility regionally, and yields of different raw materials mixed with CM were researched for establishing biogas plants.

3.3.1.1.Composition of a biogas plant

A biogas plant generally consists of components including storage & treatment for both feedstock and digestate, digestion unit, gas storage, pipes and pumps (for gas transport), and gas utilization (Baxter et al. 2013). Materials needed for constructing a biogas plant depend on chemical and biological characteristics of the feedstock or biogas; scales of the plant elements are determined by quantity of feedstock or biogas; and a well performed plant relies on the suitable technology and correct engineering (Baxter et al. 2013). To calculate electrical power installation of a biogas plant mainly fed by CM, it is suggested to multiply daily manure volume by 2.4 kW_{el} d/m^3, and typically a farm of 200 cows produces about 10 m^3/d manure containing 10% dry matter content (Seadi et al. 2008). Therefore, for a farm of 200 cows, the power installation is about 10 m^3/d * 2.4 kW_{el} d/m^3 = 24 kW_{el} (kilowatt hours electrical energy). Certain factors are needed to consider locating a biogas plant, such as distance from residential areas, majority wind direction annually (to avoid odour disturbing residential areas), access to electricity grid (for CHP plants) or transport roads (for plants turning biomethane into vehicle fuel), and possibility of affection by flood (Seadi et al. 2008). Land area needed for a biogas plant cannot be determined simply, but based on the experience, a 500 kW_{el} plant generally requires 8000 m^2 (Seadi et al. 2008).

3.3.1.2.Raw material availability

Cow manure is available in quite wide range within Finland, which extends to northern region further than Oulu (Figure 2), and the main concentrated region is in the middle part from the western coast across Kokkola and Vaasa, reaching to Pori. As mentioned in the legend, the map mainly presents CM amount excluding the housing sources which may be widely dispersed and uneasy to obtain. Furthermore, the map is based on data of year 2017 as stated in Biomass-Atlas website.

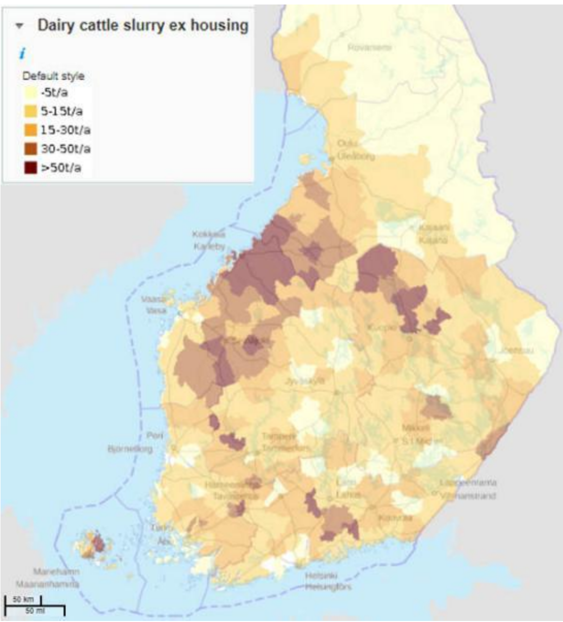

Figure 2. Cow manure distribution in Finland (Biomass Atlas 2020a).

Unlike CM distribution, grass availability is more dispersed in the lower half land of the country, and appears denser in the bottom south (Figure 3). In the map four types of items are included, which are grass seed production byproduct, grass seed production cultivation area, reed canary grass biomass yield, and grassland cultivation biomass yield. However, it is suggested to conduct some detailed survey about amount of grass that can be used for biogas production in the particular region, since it may be cultivated as feedstock for livestock industries around.

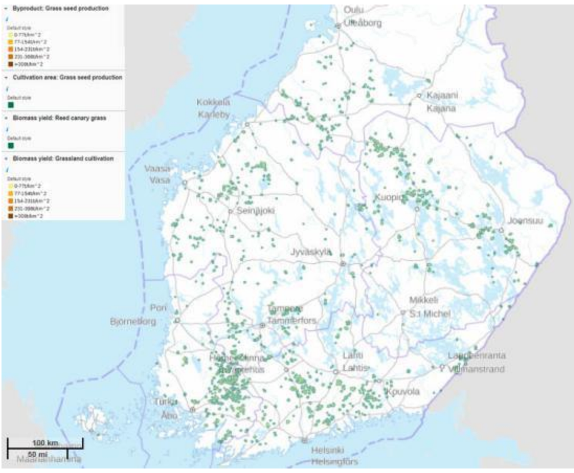

Figure 3. Grass biomass distribution in Finland (Biomass Atlas 2020b).

Oat (*Avena sativa*) production concentrates in western and southern regions of Finland generally, from Oulu at north to the sea shore in south, and from western sea shore to Jyväskylä in the middle horizontally (Figure 4). Oat distribution is mentioned here, is due to the high methane yield by its straw while being mixed with CM for co-digestion, which is introduced later on in the methane yield (3.3.2) section.

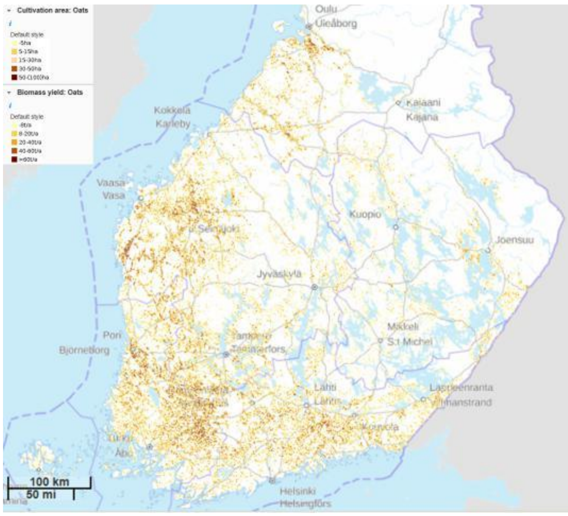

Figure 4. Oat biomass distribution in Finland (Biomass Atlas 2020c).

There are other types of biomass cultivated or naturally growing in considerable scales within the country, since the research project favours co-digestion of CM and grass, only availability of CM and grass are focused in this study, and oat is researched as an example for an alternative in case grass is unreachable in some particular regions. Distribution information of domestic biowaste and industrial biowaste derived from animals and plants through processing factories can also be found in Biomass-Atlas with the link mentioned above in the caption of Figure 4.

3.3.2. Biogas yields by different raw materials

According to Buswell and Mueller (1952), it is possible to estimate 95-100% yields by calculation through equation (1) mentioned previously, and calculation of the equation is conducted using atom numbers of C, H, and O. Hence, the major contents of biowaste such as carbohydrates may yield 830 m^3 Mg^{-1} VS biogas containing 50% methane, fat 710 m^3 Mg^{-1} VS biogas with 70% methane, and protein 920 m^3 Mg^{-1} VS biogas with 50% methane, based on which methane yield of the biowaste can be estimated by determining its organic composition (Schnürer and Jarvis 2018). However, practical results may differ from the theoretical values due to various factors affecting degradation of the organic matters and production yield of methane (Schnürer and Jarvis 2018). The difference between practical and theoretical yields may be caused by things such as certain energy may be consumed for microbial growth; incomplete degradation of organic matters; different composition of the organics such as sugars, proteins and fats; and inhibition by certain excessive individual components such as protein and ammonia (Angelidaki and Ahring 1994, Gallert and Winter 1997, Schnürer and Jarvis 2018).

Methane yield of known raw material (feedstock) can also be estimated based on previous researches conducted with similar or same combination of the substrates, considering feasibility of conducting the processes. As reported by Wang et al. (2016), wet co-digestion of CM (15.34±0.01% TS) and maize straw (92.15±0.01% TS) sampled in central China with mixing ratio of 10:3 at 37±0.5℃ for 30 days generated methane ranging from 175 m^3 Mg^{-1} VS to 378 m^3 Mg^{-1} VS with supplement of alpha-amylase enzyme. In a CSTR experiment, methane yield of CM and maize straw sampled in Central China could reach to 165 m^3 Mg^{-1} VS with mixing ratio of 10:1 through wet digestion (TS 6%) at 38±0.5℃ for 32 days (Wang et al. 2017). And in the same experiment, 175 m^3 Mg^{-1} VS methane was produced from same amount of CM and maize straw, with supplement of fruit and vegetable waste accounting for 1%, and 202 m^3 Mg^{-1} VS with 5% fruit and vegetable waste under same mesophilic condition adjusted to same TS content after same number of days.

Wet digestion from combination of CM (13.8±0.08% TS) and food waste (28±1.3% TS) sampled in San Francisco, USA could yield 282 m^3 Mg^{-1} VS methane with mixing ratio of 68%:32% under mesophilic condition at 35±1℃ for 30 days, and 311 m^3 Mg^{-1} VS at mixing ratio of 52%:48% under same digesting condition during the same days (El-Mashad and Zhang 2010). In another report, 1:1 mixture of CM (23.19±0.54% TS) and kitchen waste (14.99±0.19% TS) sampled in Northwest China produced methane ranging from 121 (at initial pH of 6.5) to 180 (initial pH 7.5) m^3 Mg^{-1} VS through semi-dry digestion under mesophilic condition of 35℃ for 45 days (Zhai et al. 2015). Oat straw sampled in Northern China as a co-substrate along with CM sampled in Central China could produce methane ranging from 158 m^3 Mg^{-1} VS (mixing ratio CM:OS 4:1 containing 10% total solids) to 416 m^3 Mg^{-1} VS (mixing ratio 1:2 containing 4% TS) through wet digestion at 37±2℃ with pH within 6.63-8.40 for 50 days (Zhao et al. 2018). Combination of CM and sugar beet tops sampled in central Finland could produce 149±12 m^3 Mg^{-1} VS through wet digestion (TS 4.9±0.1%) in a CSTR system at 35±1℃ with mixing ratio of 95%:5% for 28 days, and 229±54 m^3 Mg^{-1} VS through wet digestion (TS 5.0±0.1%) with mixing ratio of 85%:15% for 59 days (Cropgen 2006). Waste sludge collected from primary and secondary wastewater treatment processes for paper and pulp industries, has also been reported as material with high energy recovery yield (Priadi et al. 2014). CM and sludge of paper and pulp mill sampled in Indonesia with mixing ratio of 57% to 36% (the rest is water for diluting TS of CM to about 20%) could yield 269 m^3 Mg^{-1} VS through wet digestion (TS 8.47%) at 29.0-32.5℃ with pH ranging from 6.2 to 7.3 for 40 days (Priadi et al. 2014).

Composition of CM and grass (seed mixture of 75% timothy (*Phleum pratense*) and 25% meadow fescue (*Schedonorus pratensis (Huds.)* P. Beauv)) silage (70%:30%) sampled in Central Finland could produce 179 m^3 Mg^{-1} VS methane through wet digestion (CM 6.5% TS, and grass 38% TS) under mesophilic condition of 35±1℃ with pH within 7.2-7.5 for 20 days (Jagadabhi et al. 2008). In another experiment, CM and grass containing 75% timothy and 25% meadow fescue which were both sampled in Central Finland could produce 143±16 m^3 Mg^{-1} VS methane at mixing ratio of 90%:10% under mesophilic condition of 35±1℃ through wet digestion (TS 4.9±0.1%) in a CSTR system for 28 days (Cropgen 2006). Additionally, Moset et al. (2017) reported that CM and chopped grass (species unknown) sampled in Denmark with mixing ratio of 95%:5% could yield 253±20 m^3 Mg^{-1} VS under thermophilic condition of 52℃ through wet digestion (TS 8.30±1.41%) at pH 7.89±0.06 in a CSTR system for 50 days. In another CSTR system of the same design maintained at same temperature in the same experiment, CM and excoriated grass (95%:5%) produced 261±15 m^3 Mg^{-1} VS methane through wet digestion (TS 7.89±1.24%) at pH 7.91±0.06 during the same days; and CM and swatted grass (95%:5%) produced 246±13 m^3 Mg^{-1} VS methane through wet digestion (8.26±1.67% TS) at pH 7.87±0.05 during the same days. Furthermore, Zheng et al. (2015) experimented that CM and switchgrass (*Panicum virgatum* L.) sampled in central China could yield 133 m^3 Mg^{-1} VS methane with mixing ratio of 3:1 through wet digestion (TS 6%) under mesophilic condition of 37±1 ℃ with pH within 6-8 for 30 days. And in the same experiment, 155 m^3 Mg^{-1} VS was reached when the mixing ratio was 2:2, with pH fluctuating within 6-8, and 143 m^3 Mg^{-1} VS with mixing ratio of 1:3 during which pH fluctuated within 5.5-8.0 under same digesting condition during the same days.

According to Himanshu et al. (2018), cattle slurry sampled from a cow farm mixed with perennial ryegrass (*Lolium perenne* L., var. Gandalf) in Ireland at 1:1 ratio, could yield 318 m^3 Mg^{-1} VS methane through wet digestion (CM TS 11.6%, grass 18.5%, substrate diluted with distilled water) under mesophilic condition of 38℃for 45 days. Additionally, the CM sample mixed (at 1:1 ratio) with red clover in the same experiment, yielded 287 m^3 Mg^{-1} VS methane through same type of digestion (CM TS 11.6%, grass 16.4%, diluted with distilled water) under same condition for same length of days. Furthermore, this experiment also indicated that methane yield increased sharply while adding the ryegrass gradually into the CM from 0 to 25% of the whole substrate, and the methane yield increasing rate could reach to 10% or higher. Red clover in the same experiment showed less significant effect than ryegrass during 0 to 25% rate, but with linear upward trend effect until it reached to 50% rate.

3.3.3. Economic efficiencies

According to the results of the research by the co-creator Huisman, for a small-scaled biogas plant based on a livestock farm of about 200 animal units, fed by raw materials consisting of CM and grass silage, internal rate of return (IRR) favours upgrading biogas to biomethane (IRR 16%) than CHP (negative value IRR) application of the biogas produced from AD. The lower IRR caused by CHP application is mainly due to high costs of biogas plant construction and grass silage production, along with inadequate incentives of selling electricity within Finland which could possibly cover the costs. Therefore, it is suggested for a cow farm-based biogas plant to purify the biogas to biomethane quality that can be injected into natural gas grid, to maintain a sustainable, economical, and environment friendly cow farming model.

3.4.Regulations related with biogas plants in Finland

According to the results of the research by the co-creator Ylinen, establishment of an AD-based biogas plant should follow regulations including *Act on Environmental Impact Assessment Procedure (468/1994)* and the *Decree on Environmental Impact Assessment Procedure (713/2006)*. In addition, an environmental permit is required for a biogas plant according to the *Environmental Protection Act (527/2014)*, along with a construction permit according to the *Land Use and Building Act (132/1999)*. For applying AD digestate as fertilizers, certain approval needs to be obtained from Finnish Food Safety Authority in advance, except for being used within the farm with no sales outwards. Production and storage of biogas should follow *Decree on the Safety of Processing Natural Gas (551/2009)*, and handling of the chemicals involved should follow *Act on Safe Processing and Storage of Hazardous Chemicals and Explosives (390/2005)* along with 855/2012 and 856/2012 decrees. Selling of fertilizers processed from digestate should follow *Fertilizer Product Act*. Moreover, application of manure and fertilizer products in agricultural sector should follow *Government Decree on Limiting Certain Emissions from Agriculture (1250/2014)*.

4. Summary of the literature review

Basics about AD is summarized in Table 1, including the digestion phases, classification, and conditions to secure biogas yield. An AD process undergoes four different phases from degradation of the organics to convert the intermediate products into biogas, in an order starting from hydrolysis and ending at methanogenesis. AD is divided into dry and wet digestions depending on the total solid content of the substrate, and semi-dry digestion is considered when the TS content is around the watershed value of dry and wet digestions which is 20%. Temperature, pH, oxygen absence and salt availability are all essential for generation of the biogas.

Table 1. Basics of anaerobic digestion. CSTR = continuously stirred tank reactor.

Item	Composition	Note	Reference
Phases in order	Hydrolysis	Complex molecular organics are hydrolyzed and degraded into simpler and smaller molecular organics (like fatty acids, glucose, and amino acids).	Maintiguer and Pires 2016, Schnűrer and Jarvis 2018, Laiq Ur Rehman et al. 2019
	Acidogenesis	Hydrolyzed products are degraded into smaller organics (such as acetate, butyrate, and ammonia).	
	Acetogenesis	Organics are degraded further into substances like acetate, molecular hydrogen, carbon dioxide.	
	Methanogenesis	Products of acetogenesis are converted into methane gas and other products and by-products	
Classification	Dry digestion	Substrate total solid content > 20% (Semi-dry digestion with TS around 20%). It has advantages such as less water consumption, lower digestate slurry generation, more concentrated nutrients, higher transportation efficiency and more efficient use of digesters. The disadvantages are difficulty in complete substrate mix, and impossibility of achieving optimal biodegradation.	Shahriari et al. 2011, Zhou et al. 2019, Li 2015,
	Wet digestion	TS < 20%. The substrate is adjusted to specific TS content before being fed into the digester, and process water may be needed for dilution, where inhibitory substances may also be diluted. CSTRs or wet single-pass digesters are commonly used for this type of AD process, with a complete mixing effect.	
Conditions to secure biogas yield	Temperature	30-40°C for mesophilic digestion, and 50-60°C for thermophilic digestion.	Seadi et al. 2008, Mao et al. 2015, Martin and Hine 2016, Montalvo et al. 2016, Yuka et al. 2016 Schnűrer and Jarvis 2018,
	Oxygen	Methane generation mainly relies on anaerobes requiring absence of oxygen, but aeration at earlier stage may improve hydrolysis performance and increase methane yield at the final stage.	
	pH	Methane production is generally realized within pH 5.5-8.5, within which 7.0-8.0 could be the optimal range, or 6.8-7.4 as suggested by some researchers.	
	Salts	Salts like sodium, potassium, and chlorine are essential for microbial growth, but they generally exist in biogas reactors naturally. It is suggested to maintain salt concentration within 35-80 mS cm^{-1}.	

Applications of AD products are summarized in Table 2, including utilization of both main product and by-product, along with certain notes in need of attention. Applications of biogas are generally for heat and/or energy production in different methods, and digestate is used mainly for nutrient recycle. Biogas after certain upgrading processing may be utilized to replace natural gas which is a type of fossil fuel, and digestate after the quality management could be used to replace mineral fertilizers. Biogas could be applied directly with minor processing practices, whereas digestate needs to undergo certain process for quality improvement before the fertilizer application.

Table 2. Application of anaerobic digestion product and by-product.

Product	Application	Note	Reference
Biogas (main product)	Direct combustion in boilers or burners.	Condensation and removal of particulates, compressing, cooling and drying of the gas may be needed.	Seadi et al. 2008, Lantz 2012, Čermáková et al. 2012, Baxter et al. 2013
	Combined heat and power units	Heat can be turned into electricity with higher economic value, and seasonal heat demand fluctuation can be adjusted by linking to the electrical grid.	
	Fuel cells	Biogas can be fed to generate electrical energy from chemical energy through some electrolyte. Solid oxide fuel cell is a well-known device of this application.	
	Upgraded biogas (biomethane)	Biogas undergoes certain purification process to reach to 95% of methane content, then it could be an alternative of natural gas and injected into natural gas grid, or used as vehicle fuel.	
Digestate (by-product)	Fertilizer	Digestate meeting quality requirement could perform similar enhancement result as mineral fertilizers, but is in need of strict quality control and management.	Guster et al. 2005, Al Seadi and Lukehurst, 2012,

Possible methane yields of mono-digestion from different substrates are listed in Table 3, in which temperature, pH, digestion type (dry or wet), and cycle interval of the AD processes are taken into consideration, although there could be other factors affecting the final yield (such as material composition and digester design) for the same type of substrates. The yield values are generally based on previous reports of specific experiments in literature, and certain theoretical values are also included for reference use. Mono-digestion required shorter duration in the experiments than the co-digestions listed later on (Table 4 and Table 5), and mono-digestions of CM and straw have been experimented with digestions within 25 days only. Mesophilic condition appeared to be more common temperature range for the digestions, for most of the experiments were conducted in temperature range within 30-40°C, except food waste digestion which was undergoing the digestion under thermophilic condition, but the methane yield was quite considerable.

Table 3. Methane yields of mono-digestion from different raw materials as reported in literature. CSTR = Continuously stirred tank reactor.

Material		Methane yield m^3 Mg^{-1} VS	Condition(s)	Interval (day)	Reference
CM		67	36±1°C Wet digestion pH 7. 25-7. 02	24	Achinas et al. 2018
		204±16	35±1°C WD (CSTR)	20	Cropgen 2006
Maize	Grains	393	40°C WD	40	Simona et al. 2015
	Stalks	234	40°C Dry digestion	40	
	Cobs	207	40°C DD	40	
Grass	Ley	290±7 - 340±4	37.5°C DD	30	Prade et al. 2019
Straw	Rice	333 (theoretical)	37±1°C DD pH 6.8-8.0	23	Yuan 2013
		178 (experimental)	37±1°C DD pH 6.8-8.0	23	
	Sugar beet top	181±9	35±1°C WD	20	Cropgen 2006
	Oat straw	138±17	35±1°C WD	20	
Food waste		353	35±1°C Semi-dry digestion pH 7.10	30	El-Mashad and Zhang 2010
		435	50±2°C DD pH 7.57(±0.13)	28	Zhang et al. 2006
Sewage sludge		255	35°C WD	30	Montañés et al. 2014
		28	55°C WD	35	

Methane yields from different combinations of CM with grass were researched (Table 4) weightily, considering temperature, pH, digestion length, digestion type, and specific means applied in the experiments. CM and grass mixed with same amount appeared as a combination of higher methane yield. CSTR could also help in obtaining higher yields, which has been applied commonly.

Table 4. Methane yields by different combination of cow manure and grass as reported in literature. CSTR = continuously stirred tank reactor.

Grass	Mixing ratio (CM:grass)	Methane yield m^3 Mg^{-1} VS	Condition(s)	Interval (day)	Note	Reference
(75% timothy, 25% meadow fescue) Silage type (Central Finland)	7:3	179	35±1°C WD pH 7.2-7.5	20		Jagadabhi et al. 2008
(75% timothy, 25% meadow fescue) (Central Finland)	9:1	143±16	35±1°C WD	28	CSTR	Cropgen 2006
Species unknown Chopped grass (Denmark)	9.5:0.5	253±20	52°C WD pH 7.89±0.06	50	CSTR	Moset et al. 2017
Species unknown Excoriated grass (Denmark)	9.5:0.5	261±15	52°C WD pH 7.91±0.06	50	CSTR	
Species unknown Swatted grass (Denmark)	9.5:0.5	246±13	52°C WD pH 7.87±0.05	50	CSTR	
Switchgrass (Central China)	3:1	133	37±1°C WD pH 6-8	30		Zheng et al. 2015
Switchgrass (Central China)	1:1	155	37±1°C WD pH 6-8	30		
Switchgrass (Central China)	1:3	143	37±1°C WD pH 5.5-8.0	30		
Ryegrass (Ireland)	1:1	318	38°C WD	45		Himanshu et al. 2018
Red clover (Ireland)	1:1	287	38°C WD	45		

Methane yields from different combinations of CM with other types of substrate (mainly biowaste) were researched (Table 5), taking temperature, pH value, digestion type (dry or wet), and digestion length into consideration, and some specific premises were also noted in the study. In general, the less CM is mixed into the feedstock, the more methane is produced. Mesophilic condition appeared to be a quite common for co-digestion of CM with other biomasses.

Table 5. Methane yields by different combinations of cow manure and other types of biowaste as reported in literature. CSTR = continuously stirred tank reactor.

Material	Mixing ratio (CM:other)	Methane yield (m^3 Mg^{-1} VS)	Condition(s)	Interval (day)	Note	Reference
Maize straw (Central China)	10:3	175	37±0.5℃ WD	30		Wang et al. 2016
		378	37±0.5℃ WD	30	Alpha-amylase enzyme.	
	10:1	165	38±0.5℃ WD	32	CSTR	Wang et al. 2017
Maize straw, fruit & vegetable waste (Central China)	CM:MS 10:1, 1% FVW	175	38±0.5℃ WD	32	CSTR.	
	CM:MS 10:1, 5% FVW	202	38±0.5℃ WD	32	CSTR	
Food waste (San Francisco, USA)	6.8:3.2	282	35±1℃ WD	30		El-Mashad and Zhang 2010
	5.2:4.8	311	35±1℃ WD	30		
Kitchen waste (Northwest China)	1:1	121	35℃ SDD Initial pH 6.5	45		Zhai et al. 2015
		180	35℃ SDD Initial pH 7.5	45		
Oat straw (Northern China)	4:1	158	37±2℃ WD pH 6.63-8.4	50		Zhao et al. 2018
(CM from Central China)	1:2	416	37±2℃ WD pH 6.63-8.4	50		
Sugar beet top (Central Finland)	9.5:0.5	149±12	35±1℃ WD	28	CSTR	Cropgen 2006
	8.5:1.5	229±54	35±1℃ WD	59	CSTR	
Paper and pulp sludge (Indonesia)	57%:36% Rest is water	269	29.0–32.5℃ WD pH 6.2–7.3	40		Priadi et al. 2013

5. Discussion

Production of methane during AD process undergoes four ordinal steps involving different types of biochemical reactions by diverse microbes from biodegradation in the earlier stage to biosynthesis in the final stage, and it is important to maintain suitable conditions for all segments to perform optimally. It is suggested to design digesters based on raw material characteristics (such as water content, initial pH, salt composition), predetermined digestion type (wet or dry), digestion temperature (mesophilic or thermophilic), method of pH buffering, and so forth. Although biogas from AD processes are applicable in various energy generation fields, for each of them there could be some additional process needed (except for direct combustion) mainly for purification or quality upgradation, and the quality requirement differs for different applications. Alternating fossil fuel (natural gas) could be the most expensive utilization of biogas requiring higher investment and technology, but with higher energy efficiency and significant environmental benefits, it is still a recommendable practice. Digestate after AD contains nutrients beneficial to soil and plants, but may also include unwanted components, therefore it is suggested to take fertilizer application into consideration at biogas plant design stage already.

5.1 Impact of AD substrates on methane yield

Other than the major factors that influence biogas yield from methanogenesis phase of an AD process, methane production may also vary depending on composition or properties of the feedstock, system structure of the digester, and application of specific supplements, as observed in the experiment results collected from literature. Furthermore, different types of substrate may also differ in biodegradation speed, resulting in slower methane production with longer digestion interval, or faster production with shorter digestion interval. Based on the mono-digestion results (Figure 5, prepared from Table 3), crop straw appears as faster digesting materials with considerable amount of methane yields, among which rice straw has the highest yield theoretically within 23 days, and sugar beet top has the second highest yield but within shorter interval (20 days).

5.2 Methane yield of mono-digestion

Through mono-digestion of the raw material from the biomasses selected above, the highest methane yield under mesophilic condition could reach to 393 m^3 Mg^{-1} VS by maize grains in 40 days, and the lowest yield among them was 67 m^3 Mg^{-1} VS from CM in 24 days (Table 3). Maize grains producing the highest yield is for no surprise since it is the most common energy crop of high biomass yield for biomethane production (Amon et al. 2007). CM producing the lowest yield is because the manure is already in residue phase excreted by animals after internal digestion that extracted a portion of nutrients, but the remaining microbes in the residue would contribute biodegradation of the organic matters during AD processes (Hannu Mikkola, University of Helsinki, oral teaching, 16 December 2019). However, different CM sample in different design of digesters may increase the methane yield, as the CM sampled from Finland digested in a CSTR system produced quite higher methane yield than the CM from Netherlands digested with no CSTR system. Furthermore, as stated by El-Mashad and Zhang (2010), the difference in the methane yield in the digestion experiments of food waste (10^{th} and 11^{th} columns in Figure 5) was due to composition and biodegradability of the food waste in the substrate.

Under thermophilic condition, the highest methane yield could reach to 435 m^3 Mg^{-1} VS by food waste in 28 days, and the lowest was 28 m^3 Mg^{-1} VS by municipal sewage sludge in 30 days (Table 3). It is worthy of notice that digestion under thermophilic condition requires more heat to maintain the performance. Municipal sewage sludge produced quite less methane than other materials, which could attribute to the complex process of the wastewater plant that degrades or eliminates the organic matters at the primary and secondary phases before the final sludge formation (Hopcroft 2014). In addition, it is surprising that there is a large gap of methane yields (2^{nd} and 1^{st} last columns in Figure 5) between mesophilic and thermophilic digestions of sewage sludge in the experiment by Montañés et al. (2014), in an opposite direction from the food waste experiments by El-Mashad and Zhang (2010) and Zhang et al. (2006) which resulted in higher yield in thermophilic condition (4^{th} and 3^{rd} columns in the same figure). Taking digestion length into consideration, the best material could be food waste through thermophilic digestion in 28 days, followed by rice straw through mesophilic digestion in 23 days (Figure 5). Moreover, it was unclear that whether dry digestion or wet digestion has been the dominant digesting type for mono-digestion based on the experiments selected from literature, unlike the co-digestion experiments of CM with grass and other types of biowaste in which wet digestion has been applied quite frequently (Table 3, 4, and 5).

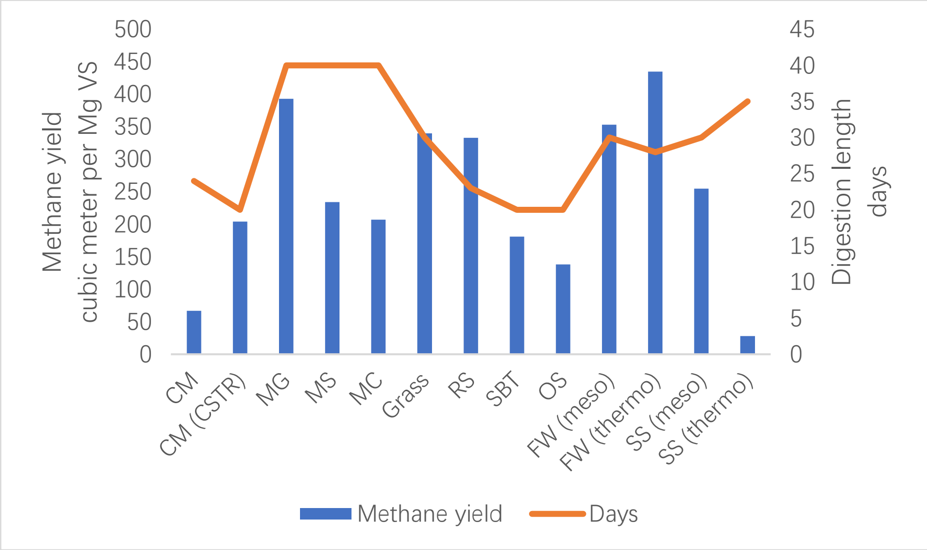

Figure 5. Methane yield of mono-digestion of different raw material (based on Table 3). CM = cow manure, MG = maize grains, RS = rice straw, SBT = sugar beet top, OS = oat straw, FW = food waste, SS = sewage sludge, meso = mesophilic, thermo = thermophilic.

5.3 Methane yield of co-digestion of CM and grass

Methane yields vary with different combinations of CM and grass of various species, digestion condition, and duration (Figure 6, drawn based on Table 4). Combination of (1:1) CM perennial ryegrass may appear as the very combination with highest yield, but the digestion interval (45 days) was within the longer duration group among the selected results. Combination of CM and switch grass at 3:1 mixing ratio appeared with the lowest yield, but the digestion interval (30 day) was within the shorter duration group (Figure 6). Taking digestion length into consideration, the best combination of CM and grass mixing ratio could be suggested as 7:3 CM with mixture of timothy and meadow fescue yielding moderate amount of methane in shorter interval of 20 days, followed by 1:1 CM with perennial ryegrass in digestion of 45 days with highest methane yield (Figure 6). In addition, CM mixed with grass containing 75% timothy and 25% meadow fescue is also an efficient combination, which could produce considerable amount of methane in only 28 days, with the mixing ratio (9:1) that fits the feasibility condition in Finland quite well (as the preferred cow farm-based biogas plant practices by the Valio Group, Antti-Pekka Partonen, Valio, Finland, meeting discussion, 6 March 2020). Furthermore, based on CM & perennial ryegrass co-digestion result of the experiment by Himanshu et al. (2018), it is suggested to add up to 25% of ryegrass into CM digestion system for methane yield enhancement.

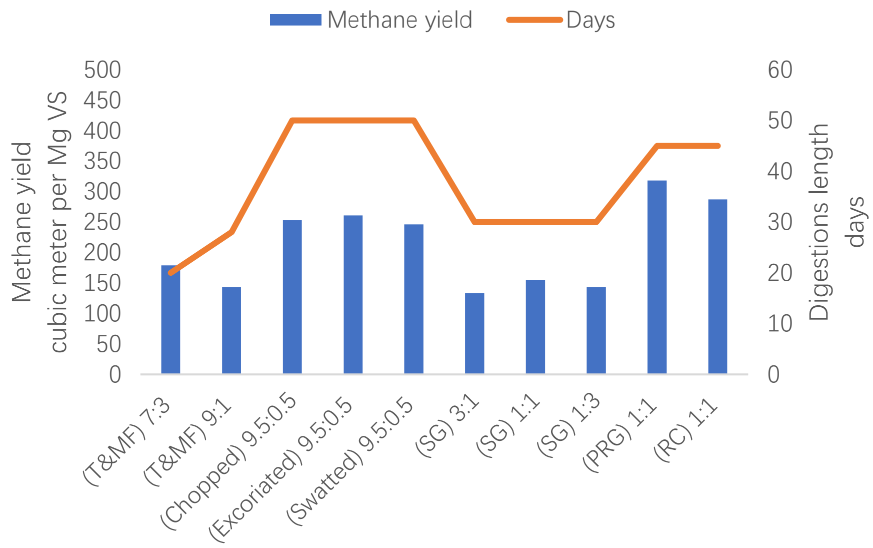

Figure 6. Methane yields by different combinations of cow manure and grass (based on Table 4). T = timothy, MF = meadow fescue, SG = switchgrass, PRG = perennial ryegrass, RC = red clover.

5.4 Methane yield of co-digestion of CM and some other common biowaste

Combination of CM with other types of biowaste resulted in wider range of yields (Figure 7, drawn based on Table 5), from the highest methane yield of 416 m^3 Mg^{-1} VS by 1:2 mixture of CM and oat straw in 50 days, to the lowest as 121 m^3 Mg^{-1} VS by 1:1 mixing rate of CM and kitchen waste in 45 days. However, either of them is quite feasible in the practical situation that CM is usually the dominant AD substrate. All the data collected for the co-digestion were about mesophilic process, indicating mesophilic-typed digestion could be the dominant AD mode in co-digestion for biogas production. Based on the collected data, the lower content of CM, the higher methane yield was produced by the co-digestion in general, except additional condition or supplement was conducted during the AD process. Taking digestion length into consideration, the enzyme supplement still appeared as an efficient enhancement means to reach to higher methane yield within shorter digestion length, indicating that adding certain type of enzyme could be an efficient method to improve methane yield (more than 100% increase from 1st to 2nd column in Figure 7). However, there is no research about adding enzyme or other supplement to co-digestion of CM with the feedstock feasible to apply in Finland (maize is a non-major crop cultivated in the country) in this study, due to absence of data obtained during the literature search. Furthermore, it may also be infeasible to apply supplement in livestock farm-based biogas plants due to the scale and investment plan or other possible reasons, therefore in this study the researches are conducted mainly for general AD practices.

Among the selected co-digestion results, CM and food waste mixed at 5.2:4.8 ratio could be the best combination with higher yield within moderate digestion length, followed by CM and food waste mixed at 6.8:3.2 ratio. However, food waste composition may vary significantly geologically, therefore it is suggested to conduct specific experiments to analyze the biogas potential for the specific sampling location. Oat straw of 1:2 mixing ratio is also a recommended combination with highest yield although during long digestion interval, but in practical situation it may be infeasible to obtain oat straw twice amount of CM, especially during non-production seasons like spring.

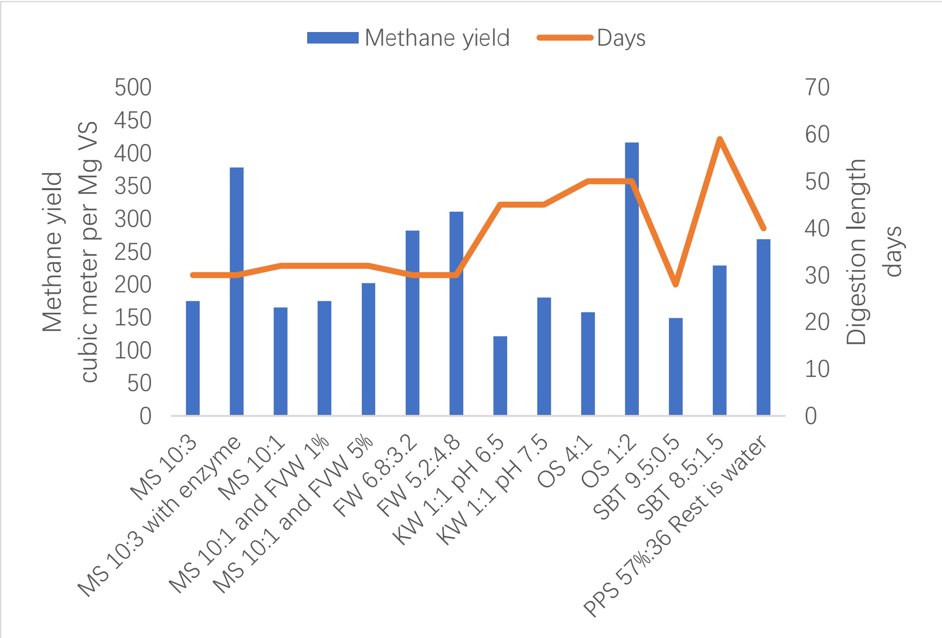

Figure 7. Methane yields by combination of cow manure with different biowastes (based on Table 5). MS = maize straw, FVW = fruit and vegetable waste, FW = food waste, KW = kitchen waste, OS = oat straw, SBT = sugar beet top, PPS = paper and pulp sludge.

6. Conclusions

For mono-digestion (taking digesting speed into consideration) of different types of biowaste, food waste could produce the highest yield but under thermophilic condition (within shorter duration) which may require more energy for heating, followed by rice straw through mesophilic condition within shortest duration. Co-digestion of CM and grass was focused in the study, and different combinations of the grass species and CM:grass mixing ratio were researched. As a result, CM mixed with grass in the amount close to half of CM is the best combination with higher methane yield within the shortest duration, followed by CM mixed with same amount of perennial ryegrass producing the highest yield within longer duration. In addition, it is suggested to supplement up to 25% ryegrass to a CM-based digester for better methane yield outcome. In case grass is unreachable, other types of biowaste available could be used for the co-digestion, CM mixed with almost same amount of food waste is the best combination with higher methane yield within shorter duration, followed by CM mixed with food waste nearly half of its amount. However, food waste in Finland may need further experiment research to estimate the methane yield. Afterwards, CM and oat straw at 1:2 mixing ratio could be another consideration, if it is possible to obtain adequate amount of oat straw. Moreover, it is also suggested to conduct certain tests for co-digestion of the planned mixture of CM and other biomass while designing the biogas plant, since composition of CM and biomass may differ from case to case, and environmental condition of the digestion system may also vary depending on the equipment facilitated in the plant, especially from the condition in laboratories.

In brief, establishment of a biogas plant involves consideration of essential premises including raw material availability, and end product outgoing solution, along with proper plan of site location, power installation, raw material combination, transport and storage of raw material and end products, and so forth. In addition, while applying grass for co-digestion with CM, environmental impacts during the whole production cycle from material flow to storage of the products (including by-product) may need certain assessment in advance. Post-production practices such as processing of the products and their transportation, may also result in some environmental effects. Economic efficiency which could be estimated with detailed survey; and legislation terms related with AD process, biogas plant composition, and AD product applications are also needed to be acknowledged to secure satisfying performance of a biogas plant. Furthermore, AD of biowaste is recommended as an efficient waste management means which also contributes to replacement of fossil fuel consumption, in an environment friendly manner.

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